Chapter 4

Supercritical Fluid–Adsorbate–Adsorbent Systems

Characterization and Utilization in Vegetable Oil Extraction Studies

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Supercritical fluid (SCF) extraction of vegetable oils from a seed matrix may require the incorporation of an adsorbent bed to remove odoriferous compounds from the recycle gas stream. In this study, an elution pulse chromatographic technique has been developed which allows the determination of breakthrough volumes (BTV) for an array of odor-causing sorbates on Tenax-TA, XAD resins, and activated carbon adsorbents. Data taken over a 100-400 atmosphere range at three different temperatures indicate that the adsorbent retention capacity is rapidly lost at pressures beyond 200 atmospheres. In specific cases with the synthetic polymer sorbents, the supercritical carbon dioxide changes the sorption capacity of the resin phase by altering the physical morphology of the sorbent. Differential heat of adsorption measurements suggest that modification of the gas-solid interface by the supercritical fluid is enhancing migration of the sorbates through the column bed. Calculations incorporating the derived BTV data base illustrate how conditions can be altered to improve trapping efficiency by varying the fluid pressure, temperature, flow rate, and sorbent charge.

Adsorption as a complementary process to supercritical fluid extraction confers an extra degree of flexibility in segregating and fractionating solutes dissolved in the fluid phase. Literature citations of adsorption coupled with supercritical fluid extraction range from the "classical" caffeine extraction with CO_2 (1) to recent attempts to separate cholesterol from butter using adsorbent beds of charcoal and silica gel (2). Prior studies utilizing adsorbents in the presence of supercritical fluid media have been reviewed by King (3), who has commented on the lack of fundamental knowledge on adsorbate(sorbate)/adsorbent(sorbent)/supercritical fluid systems. Indeed, with the exception of the sorbent regeneration studies performed at Critical Fluid Systems in the last

decade (4,5), there is a paucity of data on how industrially useful compounds behave in a supercritical fluid process stream passing through a sorbent column.

The determination of adsorption isotherms, adsorption coefficients in the Henry's Law region, heats of adsorption, along with the breakthrough characteristics of sorbates provide a basis for enlarging our theoretical understanding of the adsorption process and contribute to the design of adsorbent units operating under high pressure. Data such as the breakthrough volume characteristics of a sorbate partitioned between an active sorbent and a compressed fluid phase allow the prediction of the service lifetime of the sorbent bed and define conditions which are appropriate for selectively retaining solutes from the gas phase after the primary extraction step. More recently, the utilization of supercritical gases to selectively desorb analytes from sorbent resins, such as Tenax, XAD-2, and polyurethane foams (6-8) suggest that additional research is needed to specify conditions which are optimal for the rapid removal of analytes from these purified sorbents. Knowledge of the breakthrough characteristics for given sorbate/sorbent pairs permits the specification of sampling protocols for trapping desired components, and conversely, allows estimates to be made of the conditions required for effective desorption of reversibly-adsorbed components. As shown in an earlier study (3), the breakthrough volume asymptotically approaches a limiting volume defined by the void volume of the adsorbent bed as the system pressure is increased, hence there is a discrete pressure range over which the adsorbent bed can be used for isolating or fractionating components which are solubilized in the supercritical fluid phase.

The present work was initiated to measure the breakthrough volumes for selected sorbates which can potentially contaminate the recycle gas stream in a continuous supercritical fluid extraction system designed for processing vegetable oils. Such components, if not selectively adsorbed, can recontaminate the residual protein meal as well as extracted oil, and contribute to inferior flavor test panel scores on both products. The data base accumulated in this study also offers guidelines for designing an appropriate off-stream analytical sampling device, based on sorbent resin methodology, for collecting and characterizing the odoriferous components in the recycled supercritical fluid stream.

A schematic of the supercritical fluid extraction system is shown in Figure 1. The system is divided into two separate pressure regions; one section usually operating at pressures between 10-12,000 psig and 80°C for extracting the oil from the seed bed and a second section between the back pressure regulator and compressor held at 2500 psig and 80°. Within this lower pressure section, the oil is precipitated from the supercritical fluid phase and the solvent gas recycled back to the compressor over a bed of activated carbon. Details of the extraction conditions and equipment can be found in earlier publications (9,10). Although the system in Figure 1 was expressly designed for the extraction of vegetable oils, it is fairly typical of many supercritical fluid extraction systems, thus the data and
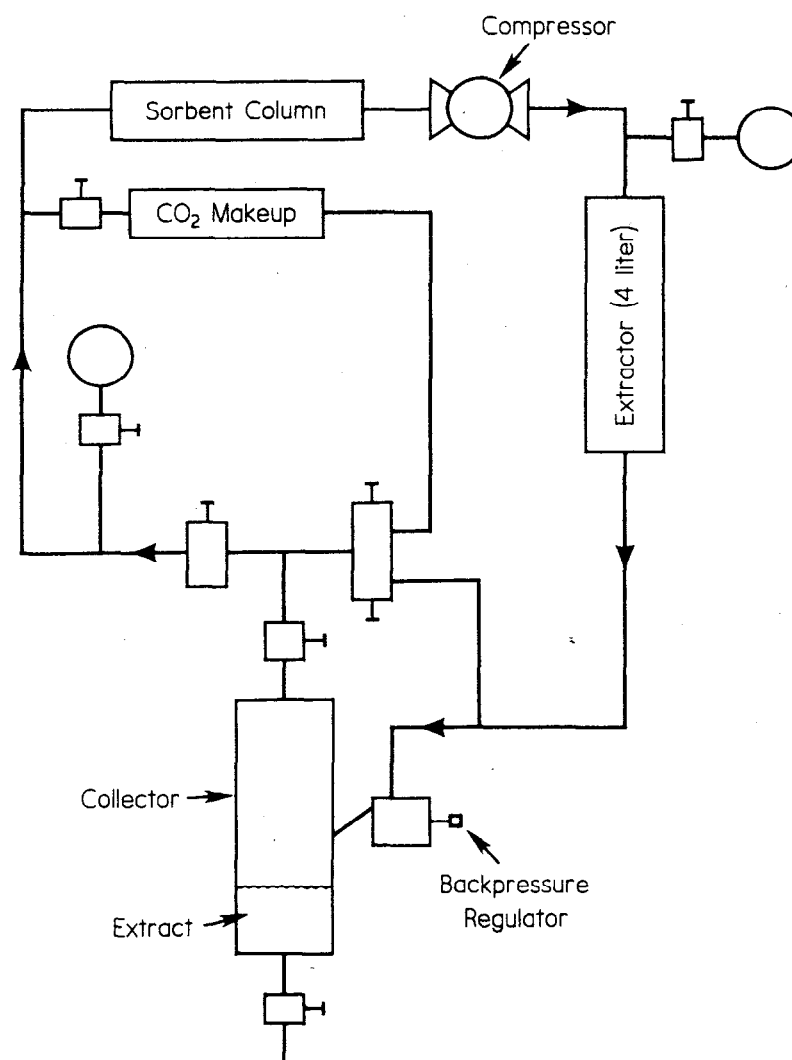
Figure 1. Continuous recycle SCF-CO$_2$ extractor.

techniques described in this paper can be extrapolated to other processing situations as required.

The technique used to measure the breakthrough volumes is similar to that reported by King (3) in which a modified chromatographic apparatus is used in the elution pulse mode to measure peak maximum retention volumes as a function of gas pressure. As described previously, trace contaminents in the SCF mobile phase elute as symmetrical (gaussian) peaks when adsorption occurs in the Henry's Law region of the sorption isotherm. The peak maximum corresponds to the 50% breakthrough volume of a sigmoidal sorbate wavefront as the adsorbent bed begins to saturate with respect to the challenge concentration of the respective sorbate. This particular quasi-equilibrium retention volume is invariant with respect to the sorbate fluid concentration and column generated non-equilibrium contributions to peak spreading, and hence is a preferred and accurate measure of the breakthrough characteristics of a given sorbate/sorbent combination (11,12). Such an approach has been utilized by many investigators to determine breakthrough data required in environmental sampling (13-15), industrial hygiene monitoring (16,17), and flavor/odor characterization (18). Good agreement between the measured retention volumes and experimental breakthrough curves has been reported (11).

The advantage of the pulse chromatographic method lies in its experimental simplicity and the ability to rapidly accumulate data which characterizes the retentive behavior of adsorbates in the presence of a supercritical fluid phase. By incorporating an apparatus which is capable of duplicating the process conditions under which the adsorbent unit is operating, one can estimate the service lifetime of the adsorption column as a function of pressure and temperature. Although retention volume data alone cannot be used to elucidate the relative contribution of competing mechanisms to the migration enhancement of sorbates in an adsorption column, such information serves a practical and applied purpose as illustrated in this study. Given the current state of our understanding of supercritical fluid/adsorbate/adsorbent systems, experimental measurement of the governing physicochemical parameters may be the most efficient and reliable way of operating and designing systems for commercial use.

Experimental

A Hewlett Packard Model 1082B supercritical fluid chromatograph was utilized for the measurement of sorbate retention volumes in this study. The instrument is a modified liquid chromatograph consisting of cooled pump heads to facilitate accurate metering of liquefied carbon dioxide from a reciprocating diaphragm pump, an ultraviolet high pressure detector flow cell capable of withstanding pressures to 400 atmospheres, and a precise back pressure regulator to maintain pressure during the chromatographic analysis. This instrumental design permitted the precise determination of BTV without substantial modification to the commercial instrument. Experimental data using supercritical

CO_2 as a carrier fluid were collected over a pressure interval of 100-400 atmospheres in a temperature range of 35-90°C. Tests performed at flow rates ranging from 0.5 to 5.0 ml/min showed that the peak maximum retention volume was constant with respect to flow rate, thereby permitting extrapolation of the measured retention volumes to higher carrier velocities.

Detection of the sorbate peak after elution from the adsorption column was accomplished using a variable wavelength detector. With the exception of 2,4-decadienal, many of the solutes utilized in this research had small molar absorptivities and could only be detected in the far ultraviolet region of the spectrum. Convenient wavelengths for monitoring purposes were 215-230 nm for the carbonyl-bearing compounds and 200 nm for the n-alcohols. Injection volumes of 1.0 μL or less of the neat solute were sufficient for detection in the reported studies.

Sorbent columns fabricated within our laboratory consisted of 316 stainless steel tubes, 3 to 12 inches in length, having an internal diameter ranging from 5/16" (0.794 cm) to 7/32" (0.556 cm). The dimensions of these columns permitted adjustment of the sorbent weight to between 0.5 - 3.0 grams, and hence the retention time range that was recorded experimentally. Adsorbent weight was determined on an analytical balance both before and after the chromatographic experiments. Reproducible sorbent weights after experimental use could only be recorded after allowing overnight outgassing of the sorbent column prior to weighing.

Table I summarizes the adsorption selection incorporated into the experimental studies. Four pre-purified synthetic resin sorbents obtained from Alltech Associates (Deerfield, IL) were used along with an activated carbon sample (Union Carbide Grade 6GC) procured from our pilot plant. The coarse particle size of the selected adsorbents in conjunction with the column dimensions and experimental flow rates yielded very small pressure drops (< 2 atm) across the sorbent bed, as ascertained by inlet and outlet pressure gauges before and after the column, respectively. Because of this small pressure gradient within the sorbent column, the recorded experimental breakthrough data were taken essentially at isobaric conditions.

Table I. Adsorbent Properties

		Property	
Adsorbent	Mesh Size	Surface Area	Structure
Tenax-TA	20-35	35 m^2/g	diphenyl phenylene oxide
XAD-2	20-50	300 m^2/g	styrene/divinylbenzene
XAD-7	20-50	450 m^2/g	acrylic ester
XAD-8	20-50	150 m^2/g	acrylic
Activated carbon	10-24	>1000 m^2/g	carbon

The sorbates utilized in this study were chosen by consulting the literature on the odor/flavor characteristics of soybean oil and meal (19,20). Specific components, such as 2,4-decadienal, 2-pentylfuran, and ethyl esters have been identified as major contributors to the flavor chemistry of soybean oil by Frankel (22) and other investigators (23). These compounds and selected solutes comprising homologous series of 2-methyl ketones, aliphatic aldehydes, and n-alcohols were chosen as sorbates based upon their probable occurrence in trace quantities during the supercritical fluid process. It should be noted that many of the sorbates used in this study exhibit appreciable volatility and would be expected to have small breakthrough volumes on the sorbents cited previously.

Several tests were performed to assure that the measured retention volumes reflected sorbate retention in the miniature adsorption column. Thermocouple-based measurements of the injection valve compartment (which is mounted outside the column oven) revealed a 2°C lag in temperature from that recorded in the column oven. This small temperature difference had a negligible effect on the solute retention volume at flow rates of 0.5 ml/min and is further minimized at higher carrier gas flow rates due to prior thermal equilibration of the gas in the column oven. The contribution of instrument dead volume was assessed by measuring the retention volume of a test solute (methanol) in the chromatographic system in the absence of the adsorption column. The system dead volume was found to be less than 0.1 ml, a negligible contribution to the measured sorbate retention volumes.

Collection of the retention data was initially taken on Tenax and XAD-2 adsorbents at 150, 250, and 350 atmospheres. As experimental work progressed, additional data was taken at closer pressure intervals to better define the trend in breakthrough volume with fluid pressure. Measurement of retention volumes below 100 atmospheres was difficult, due to the "threshold pressure" solubility limit (as defined by the sensitivity of the UV detector) of the test solute probes (23). Most of the generated retention data were measured at three temperatures: 40, 60 and 80°C.

Retention volume data accumulated over a period of two weeks on a particular sorbent showed excellent reproducibility. Retention volumes could also be reproduced at a given pressure regardless of whether the data was taken by increasing or decreasing the pressure between intervals. No bias in the collected data as a function of temperature could be detected regardless of whether the measurements were made by increasing or decreasing the temperature. Multiple determinations of the specific BTV for a given sorbate on the same column yielded a standard deviation of ± 0.3 mL/gram. Prolonged use of the Tenax columns resulted in a gradual reduction in BTV for a given sorbate at a specific pressure. The reasons for this reduction in BTV will be discussed in the next section.

Calculation of the breakthrough volume is made by using the simple equation:

$$BTV = (F) (t_r) \qquad\qquad (1)$$

where F = flow rate of the supercritical fluid at column
            temperature and pressure

t_r = time from injection to the elution peak maximum

For purposes of comparing the relative retentive properties of
adsorbents, a specific breakthrough volume may be calculated by
dividing the weight of the adsorbent into the above-defined
volume. Equation 1 is relatively simple compared to the more
elaborate calculations used to determine the net and specific
retention volumes in thermodynamic gas chromatographic studies
(24).   This in part is due to the experimental design used and
the desire to have data which reflect breakthrough character-
istics under supercritical fluid conditions. Since the combina-
tion of liquid metering pumps and back pressure regulation permit
independent control of fluid flow rate and pressure in the super-
critical fluid state, there is no need to convert the measured
retention volumes to actual column conditions or a standard tem-
perature and pressure. The breakthrough volume measurements in
this study have not been corrected for the column void volume,
since over the higher pressure range, the net retention volume
would be effectively zero in many cases. For this reason and the
accompanying observation that certain synthetic adsorbents were
physically changed when exposed to supercritical fluid CO_2, we
have elected to present retention data uncorrected for column
void volume to aid in the interpretation of the experimental
data. In addition, from the perspective of sorbate holdup in the
sorption column, a solute may be retained on the adsorbent bed if
the sampling period is brief, even though it spends all of its
residence time in the supercritical fluid phase.

Results

Our initial studies focused on the measurement of breakthrough
volumes for a variety of sorbates on Tenax-TA resin, a sorbent
which can be employed in thermal desorption methods for
characterizing the trace components in the gas stream. It was
anticipated that the trend in sorbate breakthrough volume with
pressure would parallel earlier findings (3) in which the
retention volume decreased substantially at lower pressures while
attaining a constant value in the higher pressure regime.
However, as shown in Figure 2, the BTV determination at 250
atmospheres and 40°C was approximately twice as large as those
recorded at 150 and 350 atmospheres for all of the sorbates
examined. Additional data collected over the 100-400 atmosphere
range substantiated the initial findings, indicating that there
was a distinct BTV maximum occurring in the 200-250 atmosphere
region (as typified by 2,4-decadienal).

     Close inspection of Figure 2 indicates a slight fractionation
effect between the most non-volatile component (2,4-decadienal)
and the other sorbates, particularly in the lower pressure region
(100-150 atm). This "light/heavy" selectivity trend has been
observed in other gas-solid chromatography studies, particularly
for solutes comprising a homologous series (25). For the

homologues examined in this research, little individual
separation was observed beyond 150 atmospheres. In the process
situation cited previously or for analytical collection of
sorbates, separation of the individual sorbates is not required.

To further confirm and elucidate the cause of the erratic
pattern in retention behavior shown in Figure 2, breakthrough
volumes were determined for thirteen compounds at three different
pressures on the Tenax resin. As shown in Figure 3, the
individual sorbates tended to cluster around a discrete BTV at
each individual pressure, suggesting that the retention volume
trend was independent of the sorbate type. This observation
coupled with the substantial volatility enhancement factors
expected and recorded for similar solutes (26) in SCF-CO_2
support the contention that the sorbates are passing through the
adsorption column with retention volumes equivalent to the void
volume of the column bed. Such results suggest that this
reproducible retention trend for so many solutes may be related
to changes in the sorbent structure.

To test whether the retention trends on Tenax were
reproducible and invariant with respect to experimental protocol,
several select sorbates were chromatographed over several days at
three different temperatures. As shown for ethyl caproate in
Figure 4, the pattern is reproducible for data taken 2-3 days
apart at 40°C. Cycling the sorbent bed while taking individual
retention volume measurements from low to high pressures and back
(as indicated by the different symbols in Figure 4) produced no
measurable change in retention volume pattern. This confirms
that the three-fold difference in breakthrough volume in going
from 150 to 250 atmospheres is outside the limit of experimental
error. The trend in BTV with pressure for sorbates on Tenax as
typified by ethyl caproate was also observed at 60 and 80°C.
Accumulation of additional data points in the pressure intervals
between 100-150 and 175-300 atmospheres showed that the ethyl
caproate retention minimum occurred between 100-120 atmospheres
as indicated in Figure 5. The BTV maximum was once again found
to occur between 200-250 atmospheres for ethyl caproate and other
solutes, with a second BTV minimum occurring at about 275
atmospheres.

The results obtained in Figures 2, 4, and 5 can be explained
by considering the individual factors which influence the break-
through volume trends over discrete pressure ranges. Initial
decreases in the retention volume are due to the enhanced
solvation of the sorbate (solute) in the supercritical fluid
phase abetted by displacement of the sorbate from the sorbent
surface by CO_2 as the pressure is increased. This surface
effect has been documented previously (3) and recent breakthrough
curves studies by Groninger (27) for light gas components in
compressed methane on molecular sieve confirm the competitive
displacement effect. Assessment of the relative contributions of
two reinforcing mechanisms responsible for the reduction in BTV
would require data from independent solubility and adsorption
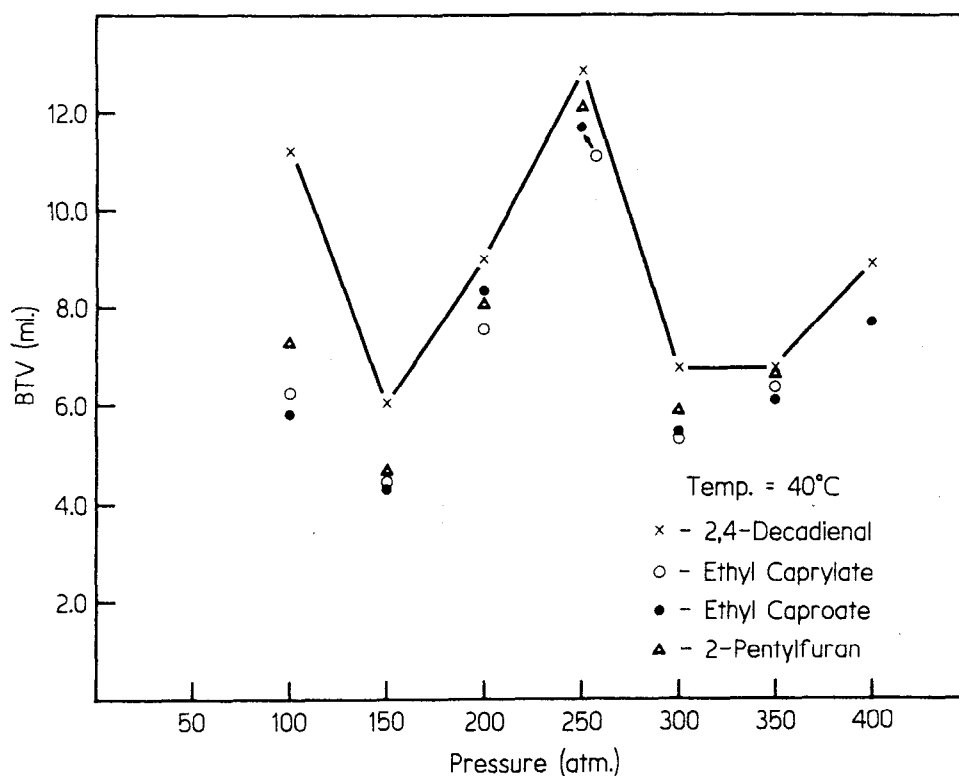experiments.

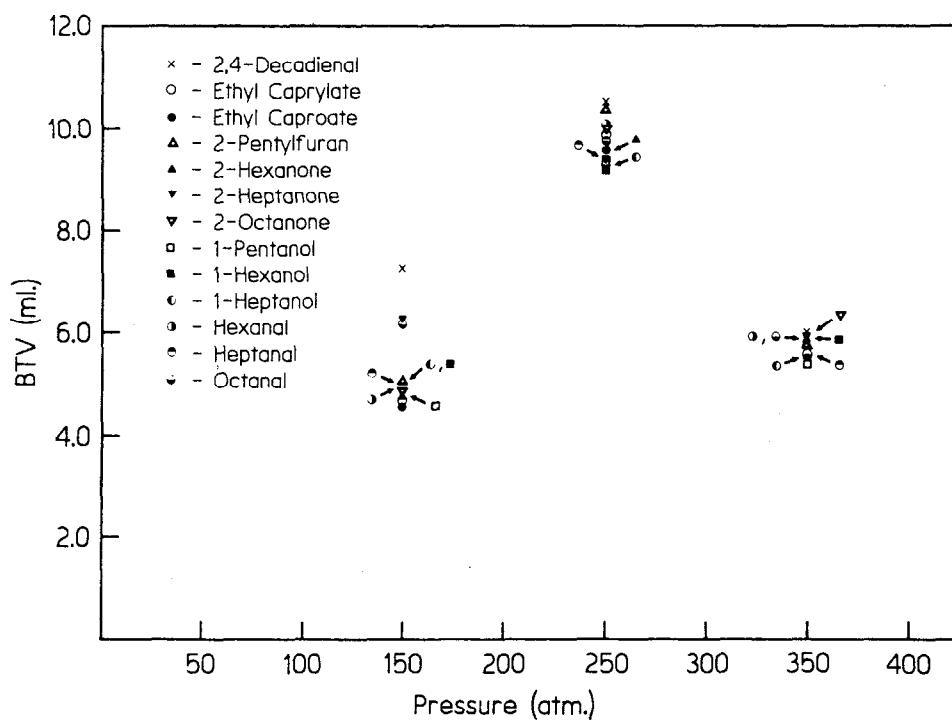Figure 2. BTV pattern as a function of pressure on Tenax.

Figure 3. BTV for a large number of adsorbates versus pressure
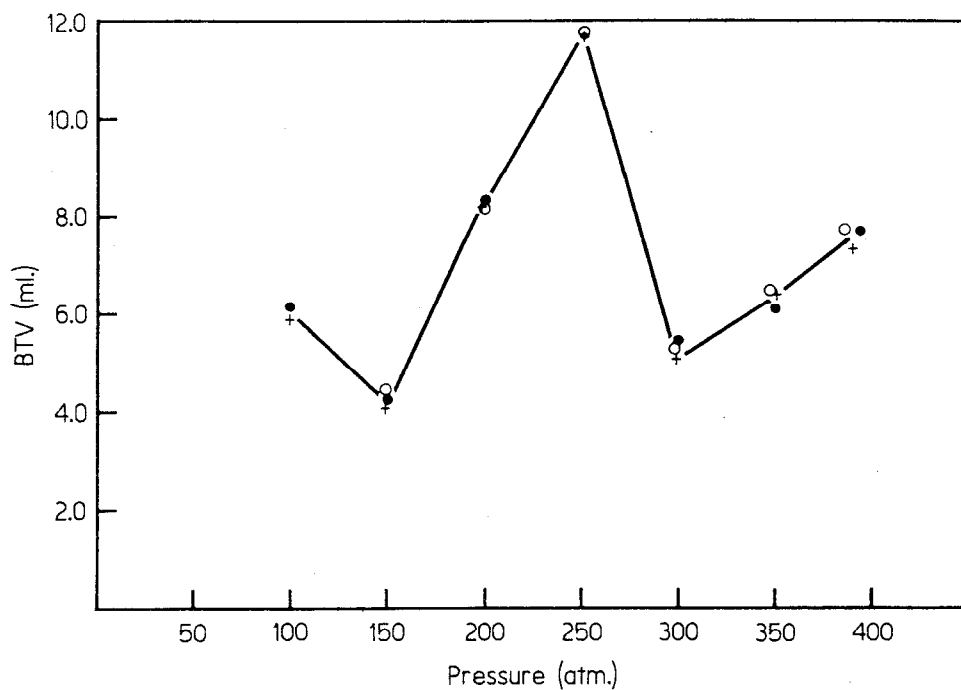on Tenax at 60°C.

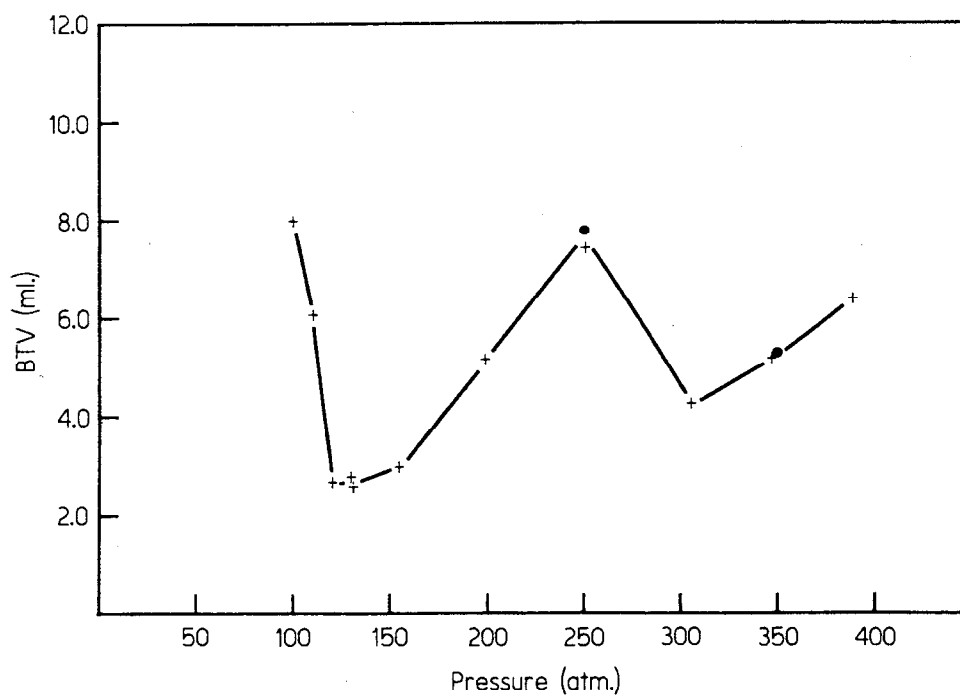Figure 4. BTV for ethyl caproate as a function of pressure on Tenax at 40°C.

Figure 5. BTV for ethyl caproate as a function of pressure on Tenax at 80 °C.

The increase in BTV at intermediate pressures for the sorbate/Tenax systems is primarily due to morphological changes in the synthetic resin sorbent. Increases in column void volume reflect a change in the internal porosity of the resin which will increase the available surface area for sorbate/sorbent interaction. Carbon dioxide has been shown to induce swelling in coal leading to higher recorded surface areas for the coal matrix (28). It is also well known that many elastomers in compressed gases (29) as well as cross-linked resins in liquid solvents (30) will swell appreciably depending on the magnitude of the solvent (SCF)-polymer interaction. Recent studies on polymethylmethacrylate polymer (31) show that dimensional changes equivalent to 16% of the polymer's original length can be affected by imbibing the polymer lattice with compressed CO_2. Plastization of similar polymers by compressed gases can also cause the glass transition temperature, T_g, of the bulk polymer to be lowered (32), resulting in physical deformation of the resin. It should be noted that the solubility parameter of CO_2 at 250 atmospheres and 40°C is 7.7 cal$^{\frac{1}{2}}$/cm$^{3/2}$, a value equivalent to many liquid hydrocarbon solvents commonly used in polymer swelling studies.

At pressures approaching 300 atmospheres, the BTV for sorbates on Tenax again decrease inferring that the dense gaseous environment surrounding the resin is less capable of inducing swelling in the polymer matrix. A similar trend in chromatographic measured void volumes has been noted by Novotny (31,34) for helium injections into a SCF-CO_2/surface-bonded silicone polymer capillary column system. Chromatographic void volume measurements may offer an alternative method to assess solvent-induced polymer swelling, provided the polymer is not miscible with the supercritical fluid.

Similar measurements to those discussed above were performed on a cross-linked styrene/divinylbenzene polymer, XAD-2, using selected sorbates. The breakthrough volume trend at 40°C for four of the sorbates is shown in Figure 6. As in previous figures, the trend in ethyl caproate BTV is emphasized by connecting the data points at each consecutive pressure by a straight line. On the XAD-2 resin, ethyl caproate does not show the initial decrease in BTV between 100-150 atmospheres as recorded for sorption on Tenax. However, in the intermediate pressure range (150-300 atm), the BTV for ethyl caproate increases to twice that value found in the lower pressure regime. Experimental data taken at 150, 250, and 350 atmospheres for ethyl caprylate and 2-pentylfuran indicate that these sorbates follow a similar pattern to ethyl caproate. The aldehyde sorbate, 2,4-decadienal shows a gradual reduction in BTV with fluid pressure. Such complex retention patterns would be difficult to predict and show the value of the experimental method in determining BTV. These results also indicate that in some cases, resinous adsorbents may yield enhanced retention capacity at higher pressures.

As with the Tenax system, there is evidence here that the sorbent may be perturbed by the supercritical fluid. Wang and coworkers (35) have shown that pressurized CO_2 can severely plasticize polymers. Creep tests (36) indicate that appreciable changes in bulk polymer moduli as well as differential changes in the glass transition temperature (up to 50 to 70°C) occur at pressures under 100 atmospheres in polystyrene. Additional dilation data for carbon dioxide absorbing into polystyrene (37) support the above study and indicate that the superimposition of a polymer phase change may also influence the retentive capacity of the polymeric sorbent.

Results obtained for the same sorbates on XAD-2 at 80°C are depicted in Figure 7. In this case the sorbate retention behavior coincides with retention volume trends reported by numerous investigators in gas-solid chromatography (3). Unlike the sorbate trends recorded at 40°C over the same fluid compression range, the BTV of the compounds decrease appreciably at pressures below 200 atmospheres and approach a constant value in the higher pressure region. As illustrated, ethyl caproate shows a 4-5 fold reduction in BTV over a 100 atmosphere interval and the selectivity and retentive capacity of the sorbent for the other sorbate moieties is eliminated at pressures exceeding 200 atmospheres. Note that there is still some retention toward the sorbates at 170 atmospheres, a condition corresponding to the low pressure side of the oil extraction system. The breakthrough volume pattern for sorbates on XAD-7 and 8 at 80°C is very similar to that observed for the XAD-2 resin and a finite adsorption capacity exists at pressures below 200 atmospheres for the sorbates studied.

When adsorption studies were conducted over a prolonged time period (one month or more) on the same resin column, it was observed that a gradual reduction in the BTV occurred corresponding to 10-20% of the initial BTV value. This phenomenon was independent of the nature of the adsorbate and was particularly obvious in the intermediate pressure ranges when using Tenax as an adsorbent. The potential for resin comminution, sintering, or other physical changes in sorbent structure due to repeated cycling from low to high pressures over the duration of the experimental work could account for the above observations. Consequently, a scanning electron microscopy (SEM) study was undertaken to compare the virgin adsorbent structure with the resins exposed to supercritical fluid carbon dioxide. Electron photomicrographs of unexposed Tenax and SCF-exposed resin are shown in Figures 8a and 8b, respectively. At a magnification level of 17X, there appears to be no difference between the irregular particles of Tenax resin. Scanning over a large number of particles at an increased magnification level, 550X, revealed differences in the porosity of the virgin and exposed adsorbent. High magnification scans at 4000X (Figure 9a and 9b) showed that the unexposed Tenax had a finer porous structure while the used sorbent had less internal porosity and was morphologically different from the virgin specimen. The condensed structure of the exposed Tenax resin might have been
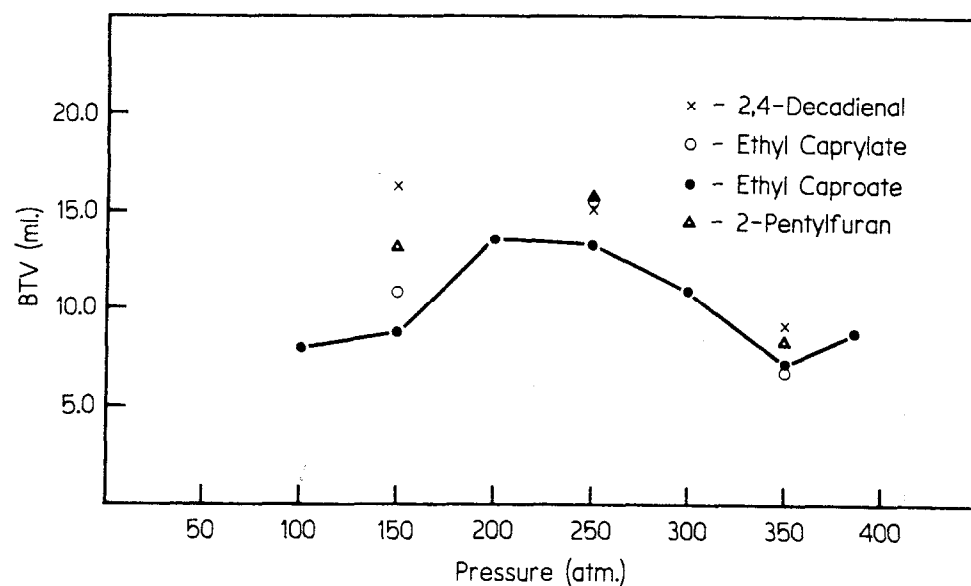
Figure 6. BTV for various sorbates on XAD-2 resin at 40°C.
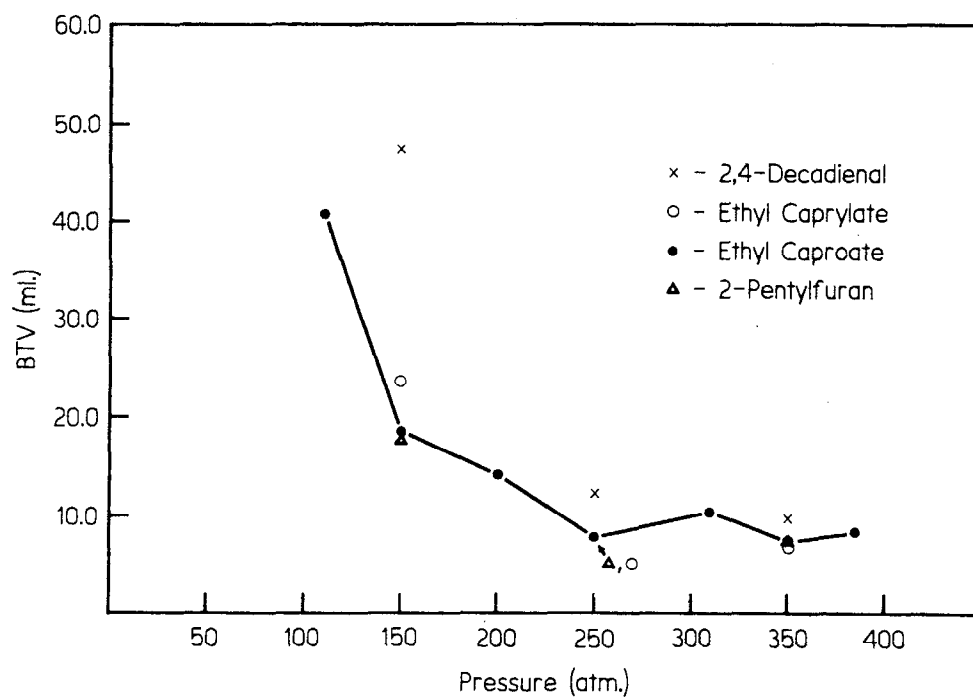

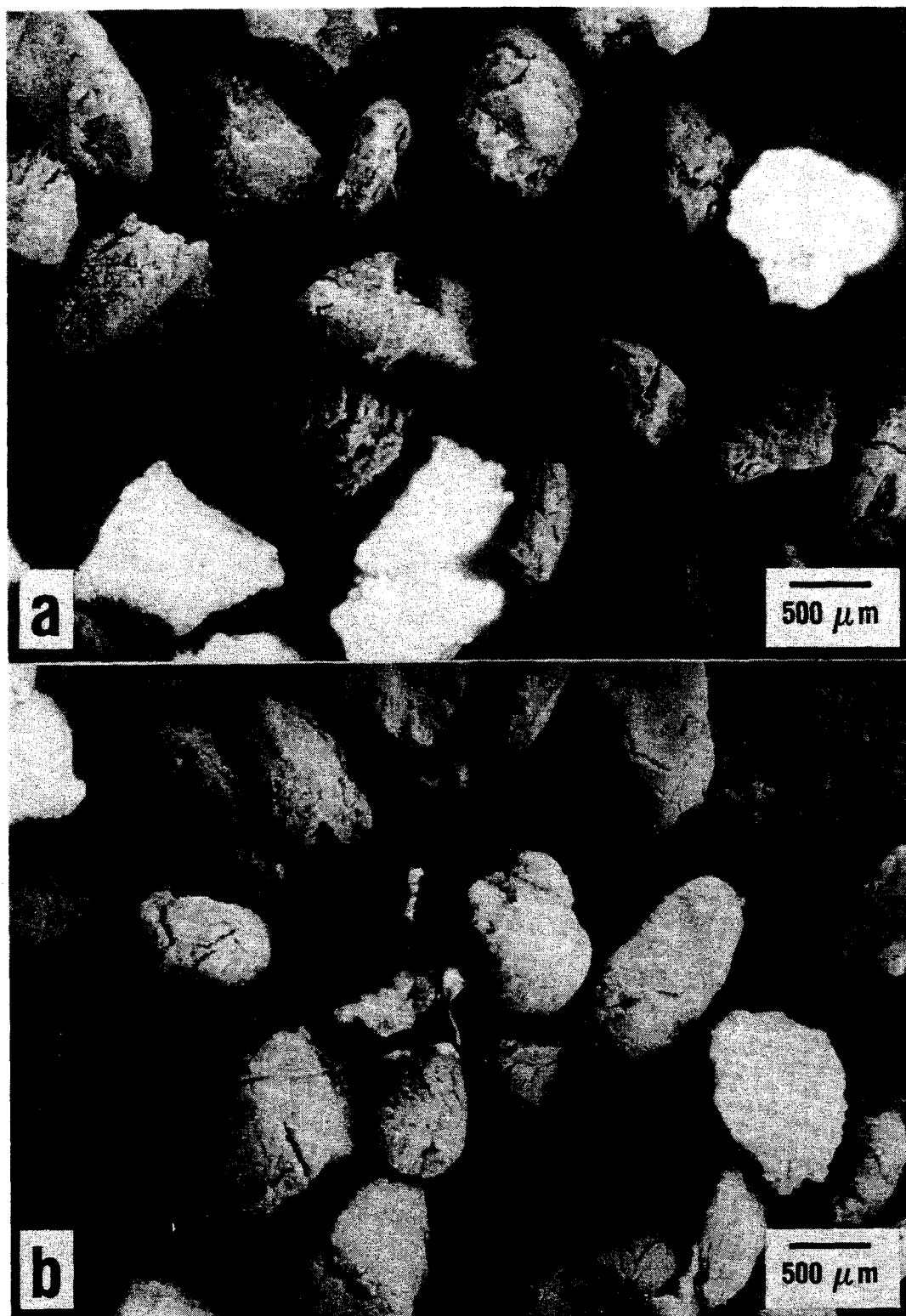Figure 7. BTV for various sorbates on XAD-2 resin at 80°C.

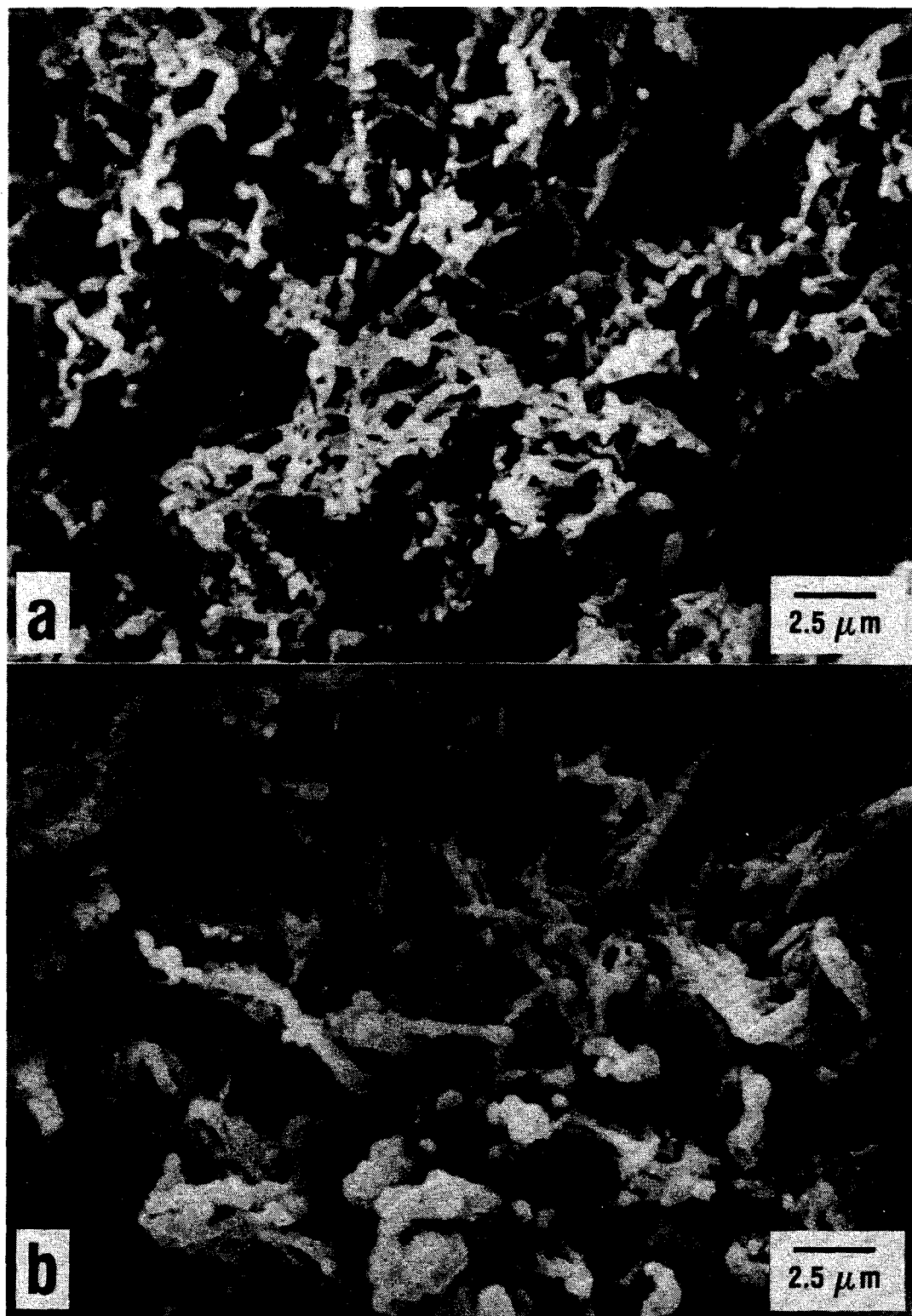Figure 8.   SEM photographs of Tenax resin (17X), (a)virgin,
(b)SCF-exposed.

Figure 9. SEM photographs of Tenax resin (4000X), (a)virgin, (b)SCF-exposed.

anticipated since chromatographic columns of the diphenyl phenylene oxide-based polymer have been shown to undergo bed shrinkage with extended analytical use.

A similar microscopic examination was also conducted on the XAD series of sorbents. Figures 10a and 10b show low magnification (27X) scans of the suspension polymerization-produced beads of the XAD-2 sorbent, which consist of aggregates of micro-particulates that comprise the spherical resin. The porosity of these adsorbents arises from the intraparticle voids between the microparticulates (38), which suggested that scans at increased magnification would be more informative. Photographs at 23,000X magnification are shown in Figures 11a and 11b for the virgin and SCF-treated sorbent, respectively. The clusters of microparticulates can be seen on the surface of the sorbent at this magnification, a pattern that was found to be consistent from bead to bead. The XAD-2 sample used for the extended BTV studies (Figure 11b) shows evidence of microparticulate sintering and an attendent loss of intraparticle porosity. The large fissures visible in Figure 11b are due to electron beam damage from the microscope's radiation source. Similar SEM studies on the XAD-7 and 8 sorbents revealed changes in their polymeric matrix morphology, however these pressure-induced alterations were observed to be less drastic due to the shorter experimental exposure times experienced by the acrylic resins.

The physical changes in adsorbent structure revealed by the scanning electron microscope studies have been observed with other polymeric materials exposed to supercritical fluids. McHugh and Krukonis (39) have demonstrated with the aid of SEM, that polypropylene preforms can be rendered porous by extraction with supercritical CO_2 and propylene. However, these investigators noted that SCF extraction of the preformed polymer sheets at higher pressures and temperatures deformed the polymer matrix leading to a fused appearance when examined by SEM and a concomitant decrease in porosity. Similar interaction between porous polyurethane foam and supercritical CO_2 reported by Smith and coworkers (7) lead to a physical alteration of the exposed sorbent. Such pressure-induced structural changes lead to a decrease in available surface area for sorbate adsorption.

Additional evidence of the role of supercritical fluids in mediating the chromatographic retention behavior of sorbates at the gas-solid interface can be gleaned from differential heat of adsorption measurements. Although only three temperatures were used in this investigation, Van't Hoff plots were constructed at pressures of 150, 250, and 350 atmospheres for the Tenax and XAD-2 sorbents. The relationships between the logarithm of the BTV and the reciprocal of absolute temperature proved to be complex and linearity was only observed for the Tenax/sorbate systems at 250 and 350 atmospheres. Non-linear behavior in plots involving the logarithm of the capacity ratio versus reciprocal of the absolute temperature have been described by Chester (40) and attributed to specific temperature regions in which the retention behavior is either gas or liquid chromatographic in
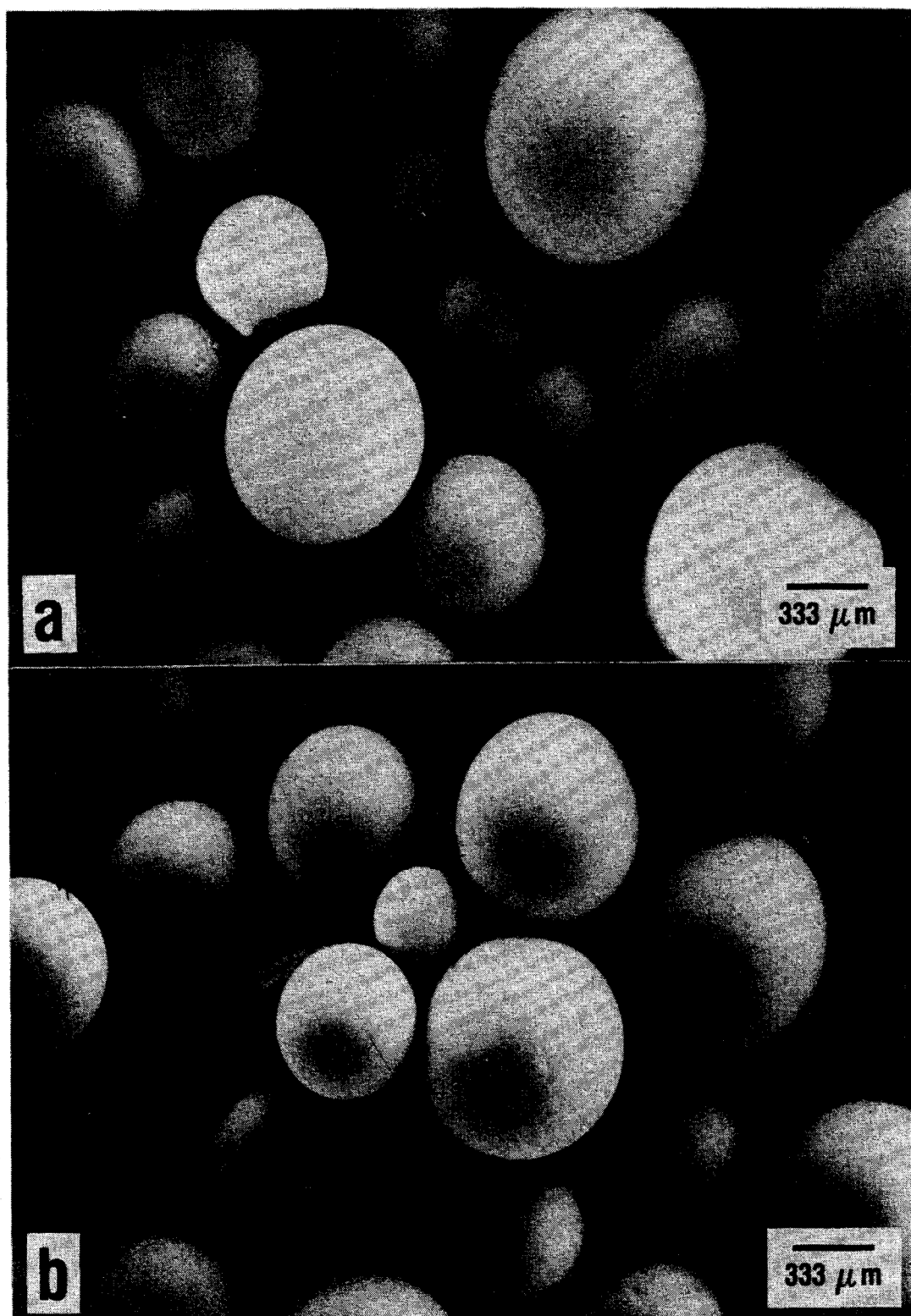
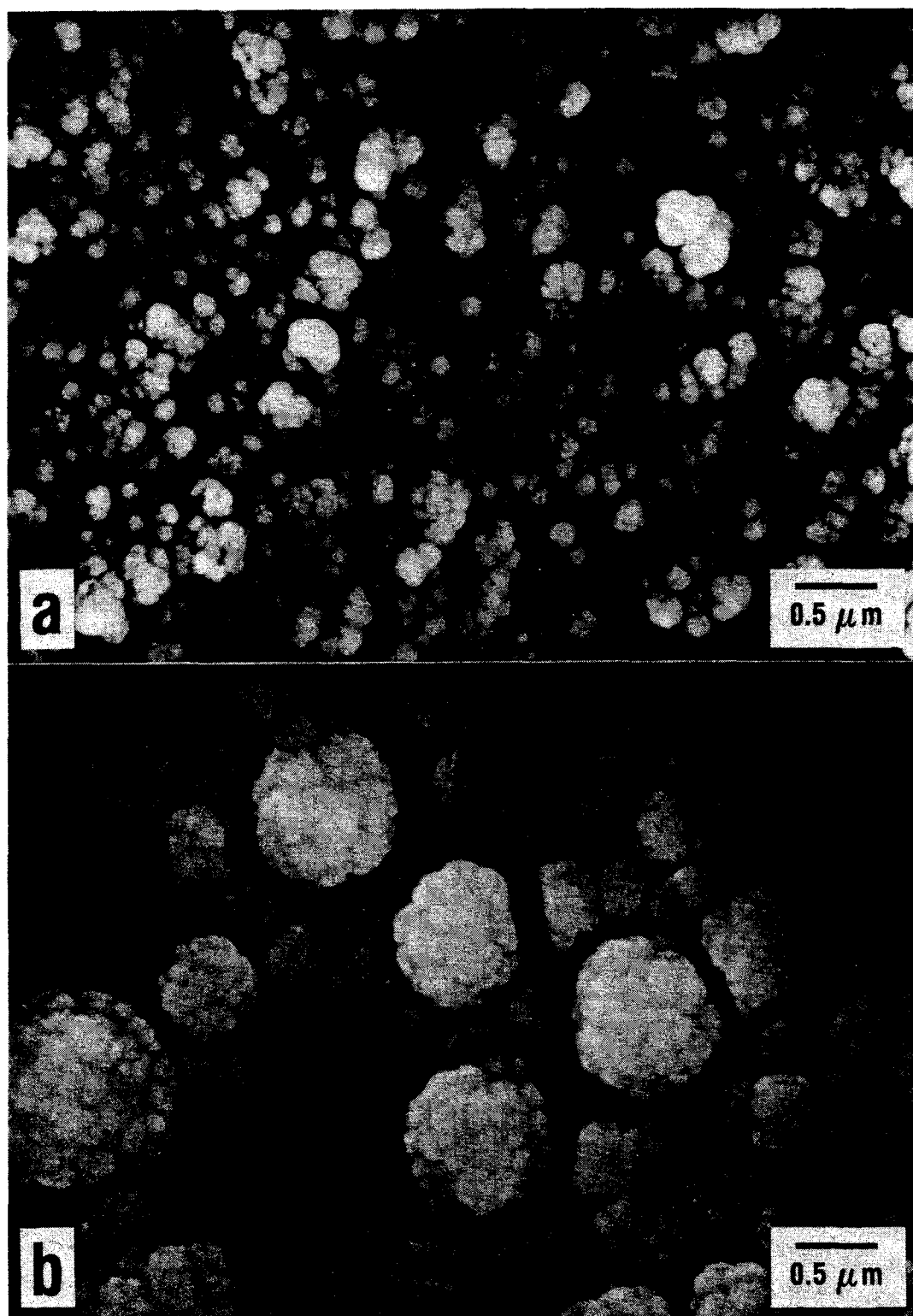Figure 10. SEM photograph of XAD-2 resin (27X), (a)virgin, (b)SCF-exposed.

Figure 11.   SEM photograph of XAD-2 resin (23,000X), (a)virgin,
            (b)SCF-exposed.

nature. Although the pressure range employed in this study is higher than that utilized in Chester's research, measurements at several other temperatures for specific solutes on Tenax at 150 atmospheres revealed a small slope change over the expanded temperature interval in the Van't Hoff plot. The Van't Hoff relationship for sorbates such as 2,4-decadienal on XAD-2 appeared to yield negative slopes at the 150 and 350 atmosphere compression levels, but changed sign from negative to positive as the pressure was decreased to 250 atmospheres. Such results may not be too surprising considering the complex array of factors which impact on the retention behavior of the sorbates. In the case of the temperature dependence of sorbates on XAD-2, the superimposition of a phase change may account for the recorded slope changes in the Van't Hoff plots. Inverse gas chromatographic studies conducted at low pressures on cross-linked styrene/divinylbenzene copolymer beads yield Van't Hoff plots with negative slopes over a rather large temperature range (41,42). As indicated previously, high pressure CO_2 can plasticize many polymers and reduce the glass transition temperature as much as 50 to 60°C. Such a pressure-induced phase change would place the T_g of the copolymer in the range of our experimental data. More experimental data needs to be taken as a function of temperature under isobaric conditions to confirm this inflection in the Van't Hoff plot.

The sorbate differential heats of adsorption per mole, $\Delta \overline{H}_A$, at higher pressures on Tenax were calculated using Equation 2:

$$\Delta \overline{H}_A = 2.303 \ R \ \frac{d \ \log \ (BTV)}{d \ (1/T)} \qquad (2)$$

where R = gas constant

   T = absolute temperature (°K)

Excellent correlation coefficients (>0.98) were obtained for the 12 sorbates on Tenax and the average differential heat of adsorption for these compounds was -1.45 kcal/mole at 250 atmospheres and -0.87 kcal/mole at 350 atmospheres. The magnitude of the heats of adsorption indicate very weak enthalpic interactions between the adsorbate vapors and the adsorbent and the recorded values are significantly less than the corresponding heats of liquefaction of the adsorbates. The almost 0.6 kcal/mole difference in the average heat of adsorption recorded at 250 versus 350 atmospheres of pressure indicates weaker interaction between the sorbates and the adsorbent at the higher pressure. Such a result is consistent with surface modification of the interface by the supercritical fluid gas (the competitive adsorption effect). An interesting comparison is afforded between the measured differential heat of adsorption for 2-heptanone absorbing on Tenax from helium close to atmospheric pressure (11) and the corresponding values on Tenax from supercritical CO_2 at elevated pressures. The differential heat of adsorption for 2-heptanone at 250 atmospheres of CO_2 is -1.42 kcal/mole and -0.84 kcal/mole at 350

atmospheres. These are considerably below the value of -19.0 kcal/mole for adsorption from a low pressure helium stream and indicative of the strong modifying effect of supercritical CO_2 on the adsorption equilibrium. A similar conclusion can also be reached by comparing the heats of adsorption determined at the above pressures for n-alcohols on Tenax.

Experiments on activated carbon as an adsorbent proved difficult due to the strong adsorbate-adsorbent interactions, which in many cases led to diffuse, non-symmetrical elution profiles and lengthy breakthrough volumes. Examination of the elution profile at 80°C and a variety of pressures allowed a qualitative assessment to be made of adsorption characteristics of various compounds on the carbonaceous adsorbent. For example, injections of ethyl caproate and 2,4-decadienal on to the carbon column at 170 atmospheres (the process condition in our recycle extractor) showed no evidence of elution after 4-5 hours from the carbon bed. The sorbate, 2-pentylfuran broke through slowly yielding a diffuse symmetrical profile. Elevation of the pressure to 250 atmospheres resulted in a more rapid elution of the furan sorbate, slow desorption of the ethyl caproate, but no elution of the 2,4-decadienal. At 370 atmospheres, breakthrough for all of the above sorbates was instantaneous and the peak maximum retention volumes were very small. Even at 370 atmospheres, complete desorption of the sorbates required elution times of over one hour. Such a technique as the one described above may have merit in monitoring the desorption of contaminents from catalysts using supercritical fluids as has been reported in the literature (43).

The results obtained on activated carbon confirm its effectiveness for trapping volatile compounds at low pressures in the presence of supercritical fluid carbon dioxide. However, reversible recovery of the adsorbed species may prove difficult due to the extremely heterogeneous surface caused in part by the presence of oxygen-containing functional groups at the gas-solid interface (44). Similar conclusions have been reached by industrial researchers attempting to use supercritical fluids for the regeneration of adsorbents (45). Recovery problems also plague the use of activated carbon as an analytical sorbent material (18).

Discussion

The determination of breakthrough volumes provides a data base for estimating the service time of an adsorbent cartridge and guide-lines for designing conditions to trap sorbates. To effectively use the experimental data; the breakthrough volumes must be expressed in volume per gram of adsorbent to correct for differences in the packing densities of the specific adsorbents. Although the conclusions from the graphical trends presented earlier remain the same, this method of presenting retention data allows for an intercomparison of the relative selectivity and trapping capabilities of candidate adsorbents. The breakthrough volume per gram also permits retention volume measurements to be

extrapolated to larger or smaller sorbent weights to fit the particular process or experimental situation under consideration.

In Table II the breakthrough volumes determined by experimental measurement or extrapolation to 170 atmospheres and 80°C are expressed as milliliters per gram of adsorbent; the conditions corresponding to the low pressure side of the recycle extractor (Figure 1). An intercomparison of these values among the four adsorbents and six adsorbates is informative since the retention volumes represent the product of the available surface area of the adsorbent and the sorbate adsorption coefficients on the trapping medium (11). For most of the sorbent-sorbate combinations in Table II, sorbate retention on Tenax resin is less than on XAD series of resins. Such a difference would have been larger (three to fourfold in some cases) had the results not been expressed in per gram of adsorbent. When individual adsorbent packing densities are taken into account, the combined effect of thermodynamic selectivity and larger surface make the XAD sorbents the preferred medium for trapping the listed sorbates. It would also appear that the sorbent surface area is the prime factor influencing the retentive capacity of the various adsorbents despite their variation in chemical structure. For example, the relatively non-polar sorbate, 2,4-decadienal is retained longer on XAD-7 then on the XAD-2 despite the polarity difference in the two crosslinked polymers. This suggests that XAD-4, another crosslinked styrene/divinylbenzene resin having a specific surface area of 725 m^2/g, may be the most preferred synthetic trapping sorbent.

Table II.   Adsorbate BTV/Gram on Selected
Adsorbent Resins

Conditions: SCF-CO_2, 170 atm., 80°C

Adsorbate	Tenax	Adsorbent XAD-2	XAD-7	XAD-8
Ethyl Caproate	2.56*	6.27	7.52	3.49
Ethyl Caprylate	3.08	7.46	7.72	4.49
2-Pentylfuran	3.01	5.78	6.27	3.99
2,4-Decadienal	5.34	15.0	22.9	12.0
2-Heptanone	3.42	3.99	6.4	3.49
Heptanal	3.15	4.48	4.4	2.76

*All figures in ml of CO_2 at 170 atm., 80°C/gram of resin

The above breakthrough volume data, including values for sorbates minimally retained on activated carbon, can be used to estimate the time for breakthrough to occur on a process sorbent

bed. For the gas recycle extractor described earlier, the number of extractions, N, which can be performed without requiring a change in the activated carbon is:

$$N = \frac{(BTV/m) \ (m)}{(F) \ (ET)} \tag{3}$$

where m = mass of the adsorbent in grams

ET = extraction time

As an example of the use of Equation 3, the BTV/gram for a limiting case, the highly volatile 2-pentylfuran on activated carbon, may be used to compute the total breakthrough volume for a 650 gram charge of carbon in the recycle stream. The specific breakthrough volume for 2-pentylfuran on activated carbon is 357 ml/gram, quite high compared to the corresponding values listed for the sorbents listed in Table II. This large breakthrough volume is reflective of the affinity exhibited by the activated carbon even in the presence of the supercritical fluid, however it is probably typical of a "light" component which would break-through rapidly compared to the other similar but less non-volatile odoriferous species. Division of the total breakthrough volume (232 liters for 2-pentylfuran) by the gas flow rate of 0.443 liters/minute (measured on-line by a mass flow meter) yields a breakthrough time of 8.73 hours. For a typical extraction run, using carbon dioxide at 0.5 lb/min for 20 minutes, this would allow over 26 extractions to be performed before the adsorbent would have to be replaced or regenerated. Using the above CO_2 flow rate and extraction time, 99% of the theoretical oil yield can be realized when extracting flaked soybean seed.

It is interesting to compare the above breakthrough volume result on activated carbon with similar data generated on one of the resinous adsorbents, XAD-7. As shown in Table III, for both a highly retained component, 2,4-decadienal, and 2-pentylfuran; the breakthrough volumes are one to two orders of magnitude smaller than for 2-pentylfuran on activated carbon using the same process conditions and sorbent charge given in the previous example. Therefore, using XAD-7 in place of activated carbon, would allow one to capture 2,4-decadienal, but not 2-pentylfuran in <u>one 20 minute extraction</u>. Clearly, for a process situation where many conditions are fixed, increasing the charge of XAD-7 may be the only convenient way of retaining the 2-pentylfuran for multiple extraction cycles. From an analytical perspective, adjustments would have to be made in either the sampling flow rate, adsorbent weight, or sampling time to trap a representative sample of the fluid phase constituents. The relatively low specific breakthrough volumes of many sorbates on synthetic resin sorbents illustrates the need for investigating alternative sorbents, particularly those which are less expensive and inter-mediate between XAD-7 and activated carbon in retentive capacity.

Table III. Comparative BTV Results for Different Sorbates
on XAD-7 Resin

	2,4-Decadienal	2-Pentylfuran
Specific BTV of sorbate	22.9 ml/g	6.27 ml/g
BTV on XAD-7 column	14.9 L	4.08 L
Breakthrough time on resin column	33.6 min	9.41 min

Conditions: SC-CO_2 Flow Rate - 0.443 L/min, 170 atm, 80°C,
Resin wt. = 650 g

Conclusions

An array of factors, such as pressure, temperature, and sorbent
type determine the breakthrough volume behavior of adsorbates on
adsorbent columns used in process engineering and analytical
chemistry. These factors contribute to the complexity of the
retention process in the presence of a supercritical fluid mobile
phase to such an extent that experimental measurement seems to be
the surest way of assessing the required data for particular
sorbate/sorbent combinations. The pulse chromatographic method
described in this publication offers a rapid and convenient
technique for determining BTV data, particularly under the
pressure and temperature conditions corresponding to the actual
processing conditions. In contrast to chromatographic elution
pulse methods conducted at near atmospheric conditions (46), the
above technique requires only an extrapolation of the retention
volume to process flow conditions.

The breakthrough volume trends for many sorbate types on the
porous polymeric sorbents indicate a limited trapping capacity in
the supercritical fluid CO_2 above 200 atmospheres. Fractiona-
tion and selective retention on these sorbents seems only
possible below this specified pressure limit for the odoriferous
solutes examined in this study. Adsorbent surface area appears
to be the most significant factor contributing to the retention
of sorbates on these sorbents as well as activated carbon. For
certain synthetic adsorbents (Tenax, XAD-2) employed in this
study, pressure-induced morphological changes in the polymer
matrix lead to an increase in the sorption capacity, and hence to
an increase in breakthrough volumes at intermediate pressures.

The breakthrough volume data base generated in this study has
application in both process engineering and analytical
chemistry. For example, it appears that the polymeric sorbents
examined in this work are unsuitable for long term processing
applications requiring elevated pressures, however by employing
the conditions and constraints defined in this study, such

sorbents could be used to characterize the constituents in a supercritical fluid process stream using analytical sorbent trapping techniques. The larger breakthrough volumes recorded for specific sorbates on activated carbon compared to the polymeric media suggests that a longer service lifetime would be realized by employing the carbonaceous sorbent. However, certain other features of activated carbon/sorbate interactions, such as irreversible adsorption at lower pressures, lengthy desorption kinetics and chemical contamination limit the analytical use of this sorbent.

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